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EFFECT OF THE CHAIN ALIGNMENT ON THE BRILLOUIN SCATTERING SPECTRA OF

HYDROSTATICALLY EXTRUDED POLYPROPYLENE

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ABSTRACT

A detailed Brillouin scattering study of hydrostatically extruded polypropylene at room temperature is carried out. The spectra obtained in various scattering configurations are used to determine the hypersonic velocity and elastic constants of the uniaxially deformed polycrystalline polymer. As polypropylene is extruded, C'_{33} increases rapidly with increasing extrusion, whereas C_{11} decreases slightly. This result reflects the increasing alignment of the polymer chain segment along the direction of extrusion. The elastic constant C_{13} decreases slightly, but C_{44} does not undergo significant change as the sample is extruded, thus indicating that the shear modulus is insensitive to the orientation of chain segments in polycrystalline polypropylene. Comparison of the Brillouin scattering results with the ultrasonic values indicate that considerable frequency dispersion in the elastic constants is present. Calculation of the orientation parameter using Mosely's theory does not yield correct results. The discrepancy indicates that Mosely's model should be used with care.

INTRODUCTION

When a high polymer sample is uniaxially deformed by extrusion it exhibits anistropic mechanical properties. It has been known for some time that the sound velocity along the draw direction increases progressively with increasing orientation, whereas the sound velocity transverse to the draw direction may decrease or remain unchanged. It is the purpose of this paper to investigate the effect of extrusion on the elastic constants in hydrostatically extruded polypropylene using the Brillouin scattering technique.

Brillouin scattering is very useful in characterizing both the equilibrium and dynamic state of polymeric materials.[1] In Brillouin scattering, light is inelastically scattered from thermal phonons to produce side bands which are shifted from the incident frequency by an amount ν given by:

$$\nu = \pm \ \frac{V}{\lambda_o} \{ n_i^2 + n_s^2 - 2n_i n_s \ \cos \theta \}^{\frac{1}{2}} \tag{1}$$

where θ is the scattering angles, λ_o is the wavelength of the incident light in vacuo, V is the acoustic phonon velocity and n_i and n_s are respectively, indices of refraction of the incident and scattering light waves.

Most previous Brillouin scattering studies of polymers deal with liquid or clear solid amorphous samples, due to the experimental difficulty associated with a very strong central elastic peak which covers up the

much weaker Brillouin side bands.[1,2] As a result, Brillouin scattering

has not been used extensively in the study of polycrystalline polymers.

However, recent development of high-contrast interferometry has alleviated

the experimental difficulty, and allows opaque samples to be studied.

In this paper, we report the Brillouin scattering study of hydro-

statically extruded isotactic polypropylene using a five-pass Fabry-

Perot interferometer system. We have examined the effect of extrusion

on the elastic constants of polycrystalline polypropylene in various

deformation states. The orientation function is obtained from the study.

This study should compliment the results of polarized Raman scattering

studies which we have reported previously.[3]

EXPERIMENTAL

The extruded polypropylene samples are kindly provided by Dr. H.

Kanetsuna. The technique of preparation has been described previously.[4]

An unextruded sample and samples with extrusion ratio (R_e) equal to

2.7, 3.0, 4.5 and 6.3, are used for the Brillouin scattering experiment.

The extrusion ratio is defined as the ratio of the cross-sectional area

of the original billet to that of final extrudate. In each sample, three

faces parallel to the extrusion axis are cut at right angles. The faces

are carefully polished with jewlers rouge to minimize surface imperfections

which can give rise to polarization scrambling of the scattered light. The

sample clarity changes from opaque in the unextruded virgin sample to trans-

lucent in the R_e = 6.3 extruded sample. A jig which is used to align the

polymer rods during cutting and polishing operations is subsequently used to hold the samples at fixed angles in the light scattering experiment.

The sample density is measured using a density gradient column. No detectable volume changes are observed in the unextruded and extruded samples. The density of all samples are found to be equal to 0.888 ± 0.003 gm/cm^3. The index of refraction of the sample is measured from the angle of critical reflectance at the base of a prism. This method gives the index of refraction to be equal to 1.49 for all samples, and is not sensitive enough to detect optical birefringence and the slight change of the index of refraction in polypropylene due to extrusion. Thus, we shall assume that n_i and n_s in Eq. (1) are equal. As a result, the sound velocity will be accurate only to 3% due to the neglect of birefringence.[5]

The Brillouin spectra are obtained using a Fabry-Perot interferometer operated in five passes. An argon ion laser equipped with an intracavity etalon tuned to a single frequency at about 4880 Å is used for excitation. The free spectral ranges used are 33 and 40 GHz and the overall instrumental finesse is over 60.

The incident laser polarization is selected with or without the use of a half-wave plate which rotates the laser polarization by 90°. The polarization of the scattered light is analyzed with a Gran-Thomson prism polarizer. Both 90° and back scattering ($\approx$180°) scattering geometries are used to obtain the Brillouin spectra.

RESULTS AND DISCISSION

We have obtained Brillouin spectra of hydrostatically extruded isotatic polypropylene in various scattering configurations. Representative Brillouin scattering spectra obtained for the sample with R_e = 4.5 using the back scattering geometry in the $x(zz)\bar{x}$ configuration and using 90° geometry in the $x(yy)z$ configuration are shown in Fig. 1. The cylindrical axis is the axis of extrusion, which is taken to be the z-axis. x and y axes are perpendicular to z. Here the Porto notation is used to denote the scattering configuration.[6] In the $x(zz)\bar{x}$ only one peak is observed while two peaks are present in the $x(yy)z$ spectrum. No detectable difference in the scattering spectrum is observed by rotating the sample about the z-axis; thus, the hydrostatically extruded polypropylene exhibits isotropic mechanical properties across the transverse plane.

The intensity of the Brillouin spectrum obtained in the $m(ij)n$ scattering configuration is proportional to the square of $\delta\epsilon_{ij}(\underset{\sim}{q})$, the change of the dielectric tensor, $\epsilon_{ij}(\underset{\sim}{q})$. Here the scattering vector, $\underset{\sim}{q}$, is determined by the propagation direction of the incident and scattering light waves designed by the indicies m and n, respectively. Since the changes in the dielectric tensor are linearly related to the strain tensor, S_{kl}, according to the expression (given in the principal axis system)[7]

$$\delta\epsilon_{ij} = -n_i^2 n_j^2 \sum_{k,l} P_{ijkl} S_{kl} \qquad (2)$$

where P_{ijkl} are Pockel's photoelastic constants, both $\delta\epsilon_{ij}$ and S_{kl} are

functions of q but the q dependence is omitted in Eq. (2) for brevity in notation.

The $x(zz)y$ spectrum has only one peak and corresponds to scattering from a longitudinal acoustic phonon propagating in the xy plane. According to Eq. (2), the intensity of this peak is proportional to P_{1133}^2 (or P_{13}^2 in the Voigt notation; the subscripts 1 and 3 refer to both xx and zz as well as the x and z axes, respectively). The spectra obtained in the $\tilde{x}(zz)\tilde{y}$ configurations yields the same information as the $x(zz)y$ spectrum due to the transverse isotropy of the uniaxial system. Here the wavy lines above x and y refer to any direction perpendicular to z; $\tilde{x}$ and $\tilde{y}$ may not be perpendicular to each other.

The two peak spectrum present in the $x(yy)z$ configuration corresponds to scattering from mixed transverse and longitudinal acoustic phonons. The intensity of the spectrum is determined by P_{12} and P_{13}.

The intensity of the $x(yx)y$ spectrum is weak compared with the $x(zz)y$ spectrum, indicating that P_{66} is small compared with P_{13}. Scattering from $x(zx)z$ is associated with P_{44}. In Table I, we summarize the relation of the change in the dielectric tensor to the strain tensor in an uniaxial system.

The hypersonic velocities of longitudinal transverse acoustic phonons propagating in various direction are determined from the Brillouin frequency shifts using Eq. (1). The results are shown in Fig. 2 as a function of extrusion ratio. In Fig. 2, the letters L and T indicate longitudinal and transverse modes respectively. QL and QT are

mixed modes, indicating quasi-longitudinal and quasi-transverse modes respectively. One notes that while the velocity of the longitudinal phonon propagating along the extrusion axis increases with increasing extrusion ratio, the velocity of the longitudinal phonon propagating in the plane perpendicular to the extrusion axis decrease slightly when the polymer is extruded to about $R_e = 6.4$.

The velocities of the various acoustic phonons propagating in a uniaxially oriented sample are completely described by the elastic constant (stiffness) matrix,

$$C_{ij} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \qquad (3)$$

where $C_{66} = (C_{11} - C_{12})/2$

The elastic constant matrix relates the stress to strain tensor by

$$T_{ij} = \sum_{kl} C_{ijkl} \, S_{kl} \qquad (4)$$

where T_{ij} is the stress tensor; in the absence of dissapation the stress tensor is related to the elastic displacement vector u by

$$\rho \, \frac{\partial^2}{\partial t^2} \, u_i = \sum_j \frac{\partial}{\partial x_j} \, T_{ij} \sum_{jkl} \frac{\partial}{\partial x_j} \, (C_{ijkl} S_{kl}) \tag{5}$$

where $i = x, y, z$.

Equations (4) and (5), together with Table I and the transverse nature of the incident and scattered light waves complete the description of the Brillouin scattering spectra of a uniaxial system.

The sound velocity curves obtained from the $z(xx)\bar{z}$ and $x(zz)\bar{x}$ scattering configurations are used to determine the elastic constants C_{11} and C_{33} by using the expressions: $V(x(zz)\bar{x} = \sqrt{C_{11}/\rho}$ and $V(z(x\bar{x})z) = \sqrt{C_{33}/\rho}$, respectively. Within the accuracy of the present experiment, the velocity obtained from the $x(zz)y$ scattering configuration agrees with that from $x(zz)\bar{x}$, indicating the consistency of the experimental result with the assumed cylindrical symmetry for the extruded polypropylene. However, a weak high frequency component also appears in the $x(zz)y$ spectrum (see Fig. 3). The frequency of this component increases with extrusion ratio but its intensity depends on scattering angle (It disappears in the $x(zz)\bar{x}$ spectrum, see Fig. 1). Since this component is not predicted by the cylindrical symmetry model, it is possible that the appearance of this peak is associated with the inherent structure of polycrystalline polypropylene. The presence of small concentration of voids may cause the effect; however, clarification of the nature of this weak component requires a further detailed study.

Elastic constant C_{44} is determined directly from the $x(zx)y$ spectrum, as the velocity associated with the Brillouin peak is equal

to $\sqrt{c_{44}/\rho}$. Knowing C_{11}, C_{33} and C_{44}, we have determined C_{13} from

the V_{Q_L} and V_{Q_T} obtained from the $x(y,y)z$ scattering spectrum, as shown

in Fig. 2, with the help of the expressions (+ for QL and - for QT):

$$\rho V_{\pm}^2 = [\tfrac{1}{2} (C_{11}+C_{33}) + C_{44}] \pm \{ [\tfrac{1}{4}(C_{11} - C_{33})^2 + (C_{13} + C_{44})^2]^{\tfrac{1}{2}} \quad (6)$$

The results for the various elastic constants as a function of

extrusion ratio are given in Fig. 4. The elastic constant C_{66} (or C_{12})

is not shown due to the fact that for cylindrical symmetry the acoustic

wave associated with the elastic constant C_{66} (or C_{12}) is not active in

Brillouin scattering.

One notes that at $R_e = 1$, C_{11} is equal to C_{13}. This result is

consistent with the fact that unextruded samples have isotropic mechanical

properties. One further notes that the elastic constant associated with

the longitudinal wave (C_{11} and C_{33}) is higher than that associated with

the transverse wave (C_{13} and C_{44}). This is easily understood from the

fact that the intrachain covalent bond is stronger than the interchain

van der Waals interaction, and the restoring forces for shear motion is much

lower than that for compression. As the sample is extruded, C_{33} rises

sharply, and C_{11} decreases gradually. The sharp rise of C_{33} and the

accompanying gradual decrease of C_{11} reflects the increasing alignment of the

chain segments along the symmetry axis as the sample is extruded. The

elastic constants C_{13} decreases slightly, but C_{44} does not undergo

significant change as the sample is extruded, thus suggesting that shear

modulus is insensitive to the orientation of chain segments. C_{13} does not

display the sharp increase at R_e = 3.5 as reported in the ultrasonic study.[8]

It is useful to compare the C_{11} and C_{33} values obtained using Brillouin scattering with the corresponding quantities obtained using the ultrasonic technique at 10 MHz.[8] The ultrasonic measurements at 190K show that C_{11} (or C_{33}) for the unextruded sample is about equal to 5.8 X 10^{10} dyn cm^{-2}. This value is slightly smaller than the Brillouin scattering value ($\approx$ 6.2 x 10^{10} dyn cm^{-2}) obtained at room temperature ($\approx$294K). At R_e = 6.4, the ultrasonic value at 190K for C_{33} is 12.4 X 10^{10} dyn cm^{-2} and for C_{11} is 3.5 X 10^{10} dyn cm^{-2}, in contrast to the room temperature Brillouin scattering values of 15.8 X 10^{10} dyn cm^{-2} for C_{33} and 5.2 X 10^{10} dyn cm^{-2} for C_{11}. Over the entire R_e = 1 - 6.4 range, the Brillouin scattering results for C_{11} and C_{33} at room temperature are consistently higher than the ultrasonic values at 190K . Since the glass transition temperature for polypropylene is about 250K, the amorphous phase at 190K is in the glass state and at 294K it is in the rubber state. Thus, because the restoring force decreases with increasing temperature, one expects that, in the absence of other mechanisms, the elastic constants at 190K should be greater than those at 294K, in contrast to the experimental results, mentioned above. The fact that the Brillouin scattering values at 294K are higher than the ultrasonic ones may suggest that the intercrystalline tie molecules show a larger restoring effect when the amorphouse region is in the rubber state. However, the temperature dependent study reported in Ref. 8 shows that over the 190 to 270K range, the velocity of the

longitudinal acoustic wave propagating along the extrusion direction decreases slightly with increaseing temperature. Thus, the greater elastic constants observed in Brillouin scattering is probably due to the presence of dispersion in the frequency range between 10MHz and 10 GHz. Since Brillouin scattering monitors acoustic phonons at considerably higher frequency (about 3 orders of magnitude higher) than the ultrasonic ones, any dispersive mechanism,if present,will render Brillouin scattering elastic constants to be higher in value. Thus, it appears that in polypropylene, the dispersion effect causing the velocity increase outweigh the softening effect due to the temperature increase.

The rise of C_{33} with increasing extrusion as polypropylene is extruded from $R_e = 1$ to $R_e = 6.4$ is about a factor of 2.6 in Brillouin scattering, in contrast to a factor of 2.1 in the ultrasonic study. This result is consistent with that obtained previously[5.8], and indicates the reinforcing effect of the intercrystalline tie molecules in the amorphous region of polypropylene is more effective in the rubber state than in the glass state.

As mentioned above, the increase in C_{33} with increasing extrusion is related to the chain segment orientation. If the deformation occurs with no change in volume, as approximately is the case in polypropylene, the increase in C_{33} is closely related to the orientation parameter.[5]

Since orientation of polymer chain segments can occur in both the crystalline and amorphous regions, deduction of the orientation function

in a polycrystalline sample using the sonic data presents some difficulty. Moreover, wide-angle x-ray data indicate that most crystalline orientation has occurred during deformation up to $R_e = 5$[5]; it is clear that the rapid increase in C_{33} with increasing extrusion reflects both crystalline and amorphous orientations.

Moseley has related the sonic velocity of oriented polymers to Herman's orientation parameter α by a simple expression,[11]

$$\alpha = \tfrac{1}{2} \, <3\cos^2\theta - 1> \; = 1 - (\frac{V_u}{V})^2 \; = 1 - \frac{C_{33}^o}{C_{33}} \tag{7}$$

where V_u is the longitudinal velocity of an unoriented sample and V is the corresponding velocity of sound propagating along the direction of orientation in an oriented sample. θ is the angle between the polymer chain axis and the direction of sound propagation, which coincides with the direction of alignment. C_{33}^o is the elastic constant of the unoriented sample.

While Eq. (7) has been shown to be useful for obtaining the orientation parameter in the amorphous phase of poly(ethylene terepthalate)[12] it is not expected to have a general applicability, due to drastic approximations introduced in devising Eq. (7).[11] To test the validity of Eq. (7) in polypropylene, we have computed the quantity $1 - \frac{C_{33}^o}{C_{33}}$, using the result given in Fig. 4. The calculated result is labelled as Brillouin in Fig. 5 together with the Herman orientation function obtained by Raman scattering for comparison.

The Herman orientation orientation was obtained from the Raman intensity measurements of the band at 1256 am^{-1}, assigned to be a CH_2

twising mode with A symmetry[3]. Since the 1256 cm^{-1} band arises from the mixture of crystalline and amorphous regions[13], the Herman orientation parameter, labelled as Raman in Fig. 5, represents the combined crystalline and amorphous orientation. The Raman result is accurate and is in fact in agreement with the orientation parameter deduced from the birefringence data. The discrepancy between the Brillouin and Raman results, shown in Fig. 5, is believed to be due to the invalidity of Eq. (7) for polypropylene.

Since the Herman orientation parameter is the average of the local orientation function of polymer chain segments,whereas the sound velocity (or the elastic constant) is a collective property, unless the pair orientation correlation effect is negligible, Eq. (7) is expected to become inadequate for approximating the Herman orientation parameter. In fact, following Born and Huang[7], it can be shown that the crystalline part of the elastic constant C_{33}^{c} is given by

$$C_{33}^{c} = \rho \left\langle \sum_{k,k'} \left(\frac{1}{m_k m_{k'}} \right)^{\frac{1}{2}} \sum_{n,l} \phi_{zz}^{kk'}(n,l) \left[z\binom{n}{k} - z\binom{l}{k'} \right]^2 \right\rangle$$

where $\phi_{zz}^{kk'}(n,l) = \left. \dfrac{\partial^2 \phi}{\partial [z\binom{n}{k} - z\binom{l}{k'}]^2} \right|_0$,ϕ being the intermolecular   (8)

potential of the crystal. m_r is the mass of the kth segment in the nth unit cell. ρ is the number density of segments in a unit cell, and the angular brackets represent the ensemble average. $z\binom{n}{k}$ is the projection of the segment k in the nth unit cell along the orientation axis. If we represent the orientation angle of $\binom{n}{k}$ segment with respect to the orientation axis by θ_{nk} and write $z\binom{n}{k} = r_{n,n} \cos\epsilon_{n,k}$, then Eq.(8) becomes

$$C_{33}^c = \rho < \sum_{k\ k'} (\frac{1}{m_k m_{k'}})^{\frac{1}{2}} \sum_{n,l} \phi_{zz}^{kk'} (n,l) [r_{n,k}^2 \cos^2 \theta_{n,k} + r_{l,k'}^2 \cos^2 \theta_{lk'}$$

$$-2\ r_{n,k}\ r_{l,k'}\ \cos \theta_{n,k} \cos \theta_{l,k'}] > \qquad\qquad (9)$$

In Eq. (9) the first two terms represent the single particle orientation functions and the second term represents the pair angular correlation. If the orientation and segment length are statistically independent, we can average the segment length $r_{n,k}$ and orientation angle separately and Equation (9) reduces to

$$C_{33}^c = \rho \{ \ \Delta < \cos^2 \theta > - \ \Delta' < \cos \theta_1 \cos \theta_2 > \} \qquad\qquad (10)$$

where Δ and Δ' result from the average over the segment lengths. θ, θ_1 and θ_2 represent the orientation angles with respect to the orientation axis. θ_1 and θ_2 are the orientation angles of the two segments which are correlated orientationally. If Δ' is positive, the pair correlation term will decrease C_{33}^c. Clearly, the second term on the right hand side of Eq. (10) is expected to make a contribution to the elastic constants on polycrystalline polypropylene; unfortunately, at present, there is no information about the magnitude of its contribution. The wide-angle x-ray diffraction study of polycrystalline polypropylene in different degrees of crystallinity is expected to provide data that can be used to evaluate the single particle and pair-correlation orientational functions.

In the above, we consider only the contribution due to the crystalline portion. To obtain the total elastic constant, the amorphous portion must

be added so that the effect of deformation on the elastic constants
of a polycrystalline solid can be accounted for. However, the microscopic
expression for the elastic constants for the amorphous material has not been
developed. It is thus premature to accept Eq. (7) as a method for the
determination of the orientation parameter for the deformed polycrystalline
polymers. Further experimental studies using techniques such as ultrasonic
or Brillouin scattering is expected to provide insight for the development
of theory to better our understanding of mechanical properties of deformed
polymers.

SUMMARY AND CONCLUSION

We have carried out a detailed Brillouin scattering study of
hydrostatically extruded polypropylene at room temperature. The spectra
obtained in various scattering configurations are used to determine the
hypersonic velocities and elastic constants of the uniaxially deformed
polycrystalline polymer. For the unextruded sample, the C_{11} and C_{33}
are equal, but as the polymer is extruded, the value of C_{33} increases
rapidly, accompanied by a mild decrease of C_{11}, thus reflecting the
increasing alignment of the polymer chain segments along the direction
of extrusion. The elastic constant C_{13} decreases slightly, but C_{44} does
not undergo significant change as the sample is extruded, thereby
suggesting that the shear modulus is insensitive to the orientation of
chain segment in polypropylene.

Comparison of the Brillouin scattering results with the ultrasonic
values indicates that considerable dispersion is present, which renders
the elastic constants at the GHz frequency to be greater than the values

at 10 MHz. The Brillouin result also supports the earlier conclusion that extrusion has a greater effect on the elastic response of the intercrystalline tie molecules in the rubber state of polypropylene. Comparison of the orientation parameter determined by the hypersonic velocity obtained from Brillouin scattering with that obtained from Raman scattering and birefringence indicates the inadequacy of Moseley's model, which relates the sonic velocity with the orientation parameter. We have pointed out the importance of pair orientation correlation which is left out in Moseley's mode. Extensive experimental work together with theory is needed to develop a reliable model for the determination of the orientation parameter from the elastic constants for the deformed polycrystalline polymer.

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TABLE I

RELATION OF THE CHANGE IN THE DIELECTRIC TENSOR TO THE STRAIN TENSOR

IN AN UNIAXIAL SYSTEM

$$\delta\epsilon_{xx} = - \epsilon_{\perp}^{2} (P_{11}S_{xx} + P_{12}S_{yy} + P_{13}S_{zz})$$

$$\delta\epsilon_{xy} = - \epsilon_{\perp}^{2} P_{66}S_{xy}$$

$$\delta\epsilon_{xz} = - \epsilon_{\perp}\epsilon_{||} P_{44}S_{xz}$$

$$\delta\epsilon_{yy} = - \epsilon_{\perp}^{2} (P_{12}S_{xx} + P_{11}S_{yy} + P_{13}S_{zz})$$

$$\delta\epsilon_{yz} = - \epsilon_{\perp}\epsilon_{||} P_{44}S_{yz}$$

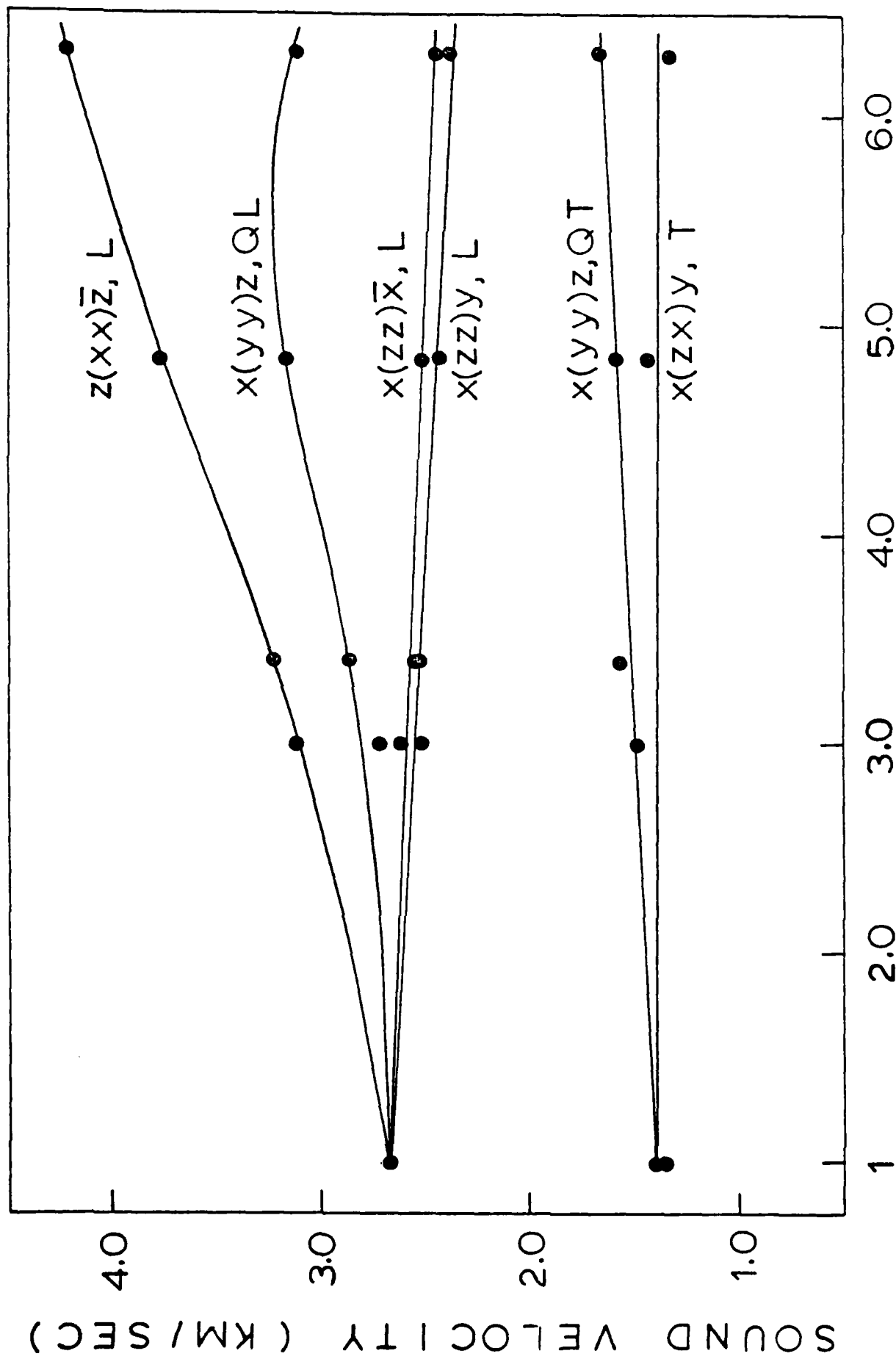$$\delta\epsilon_{zz} = - \epsilon_{||}^{2} (P_{13}S_{xx} + P_{13}S_{yy} + P_{33}S_{zz})$$

FIGURE CAPTIONS

Fig. 1   Brillouin spectra of polypropylene obtained in the
         backscattering, $x(zz)\bar{x}$, and 90° scattering x(yy)z
         configurations.

Fig. 2   The various hypersonic velocities obtained with different
         scattering configurations.

Fig. 3   Brillouin scattering spectra obtained in two x(zz)$\bar{y}$
         configurations. Note the presence of extraneous components
         indicated by arrows.

Fig. 4   The various elastic constants of polypropylene determined
         by Brillouin scattering as a function of extrusion ratio.

Fig. 5   The orientation parameter for polypropylene as a function
         of extrusion ratio as deduced from Raman (ref. 3) and
         Brillouin scattering (this work). Note the difference at
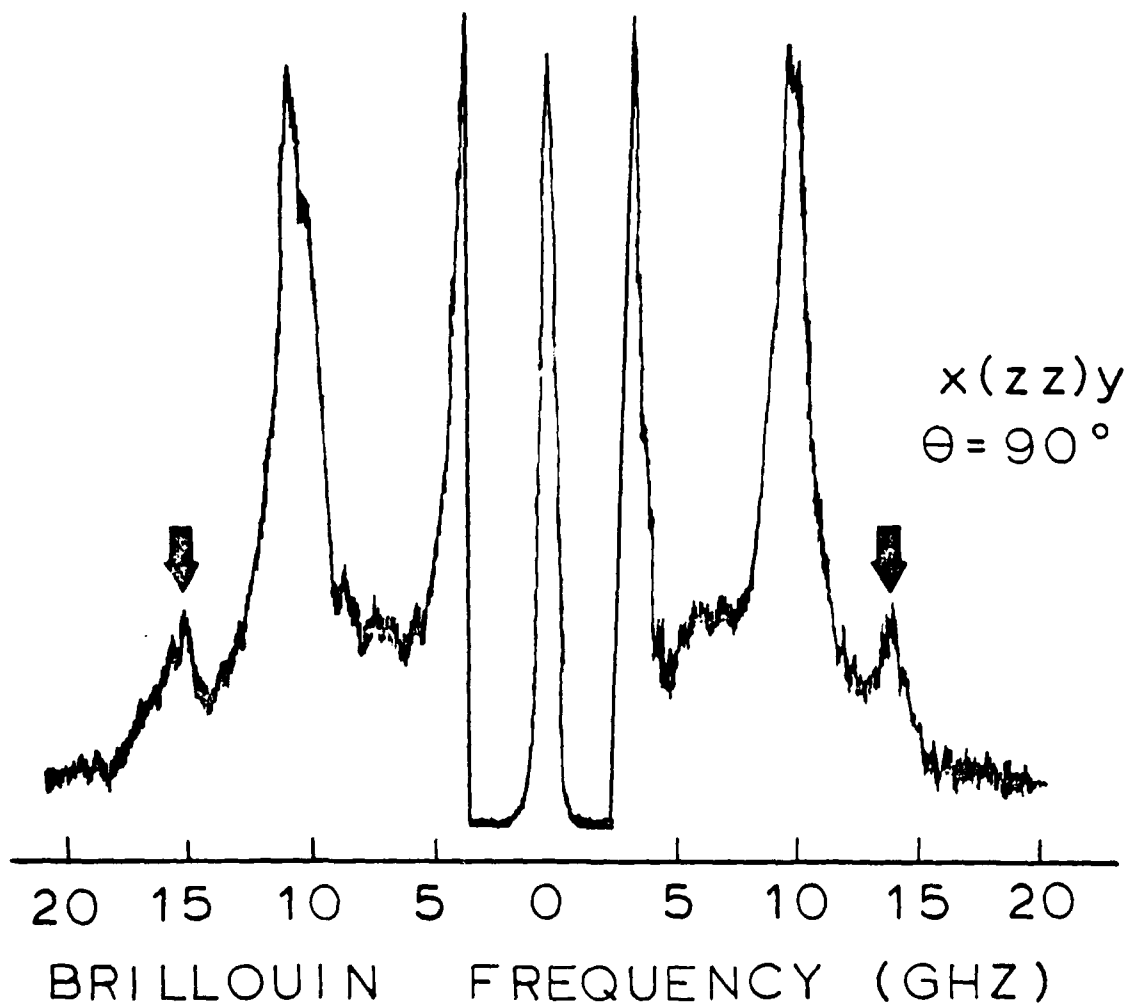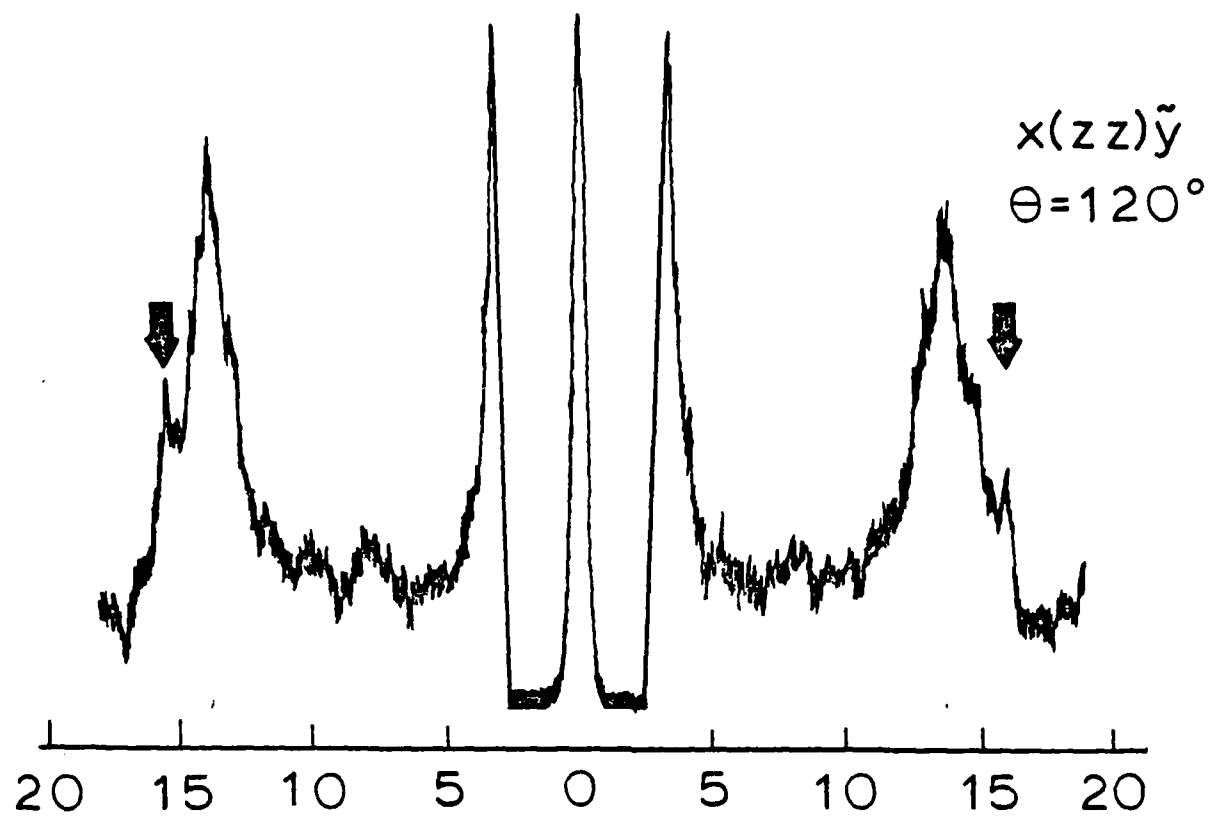   high extrusion ratio.

x(zz)x̄

x(yy)z
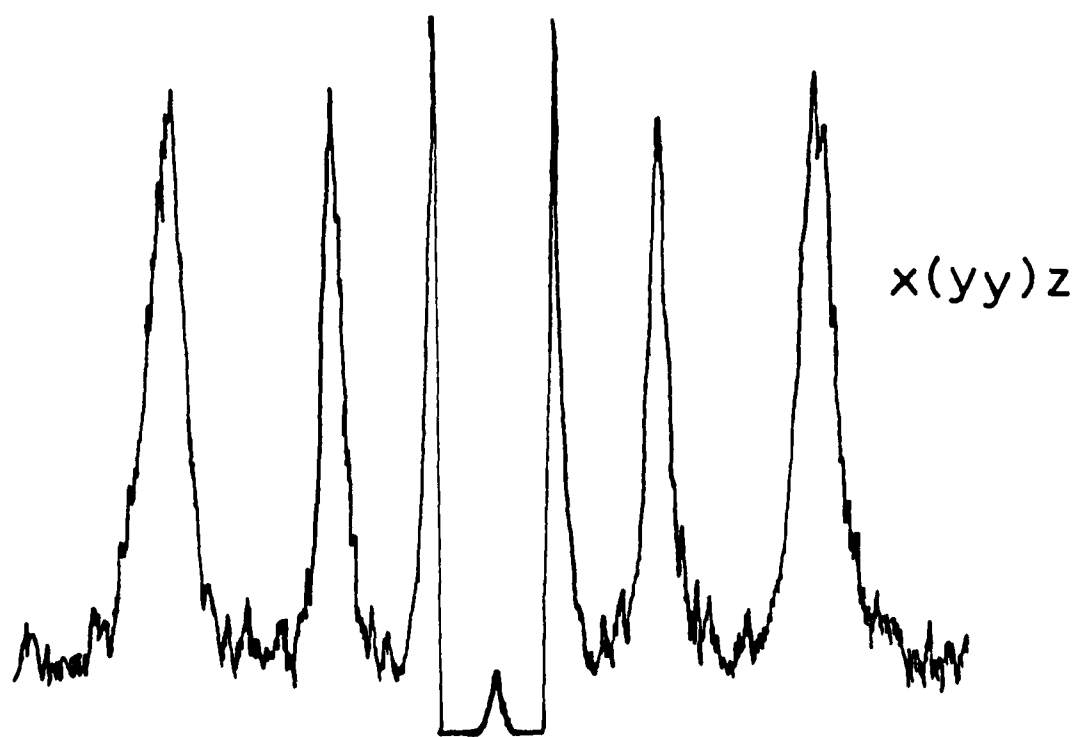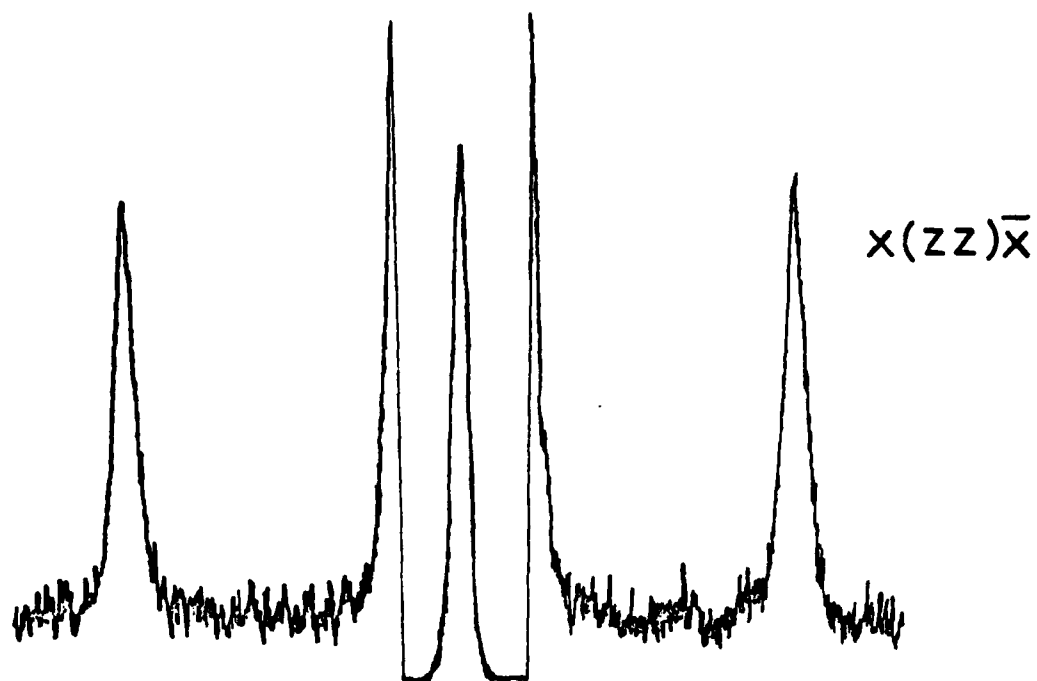
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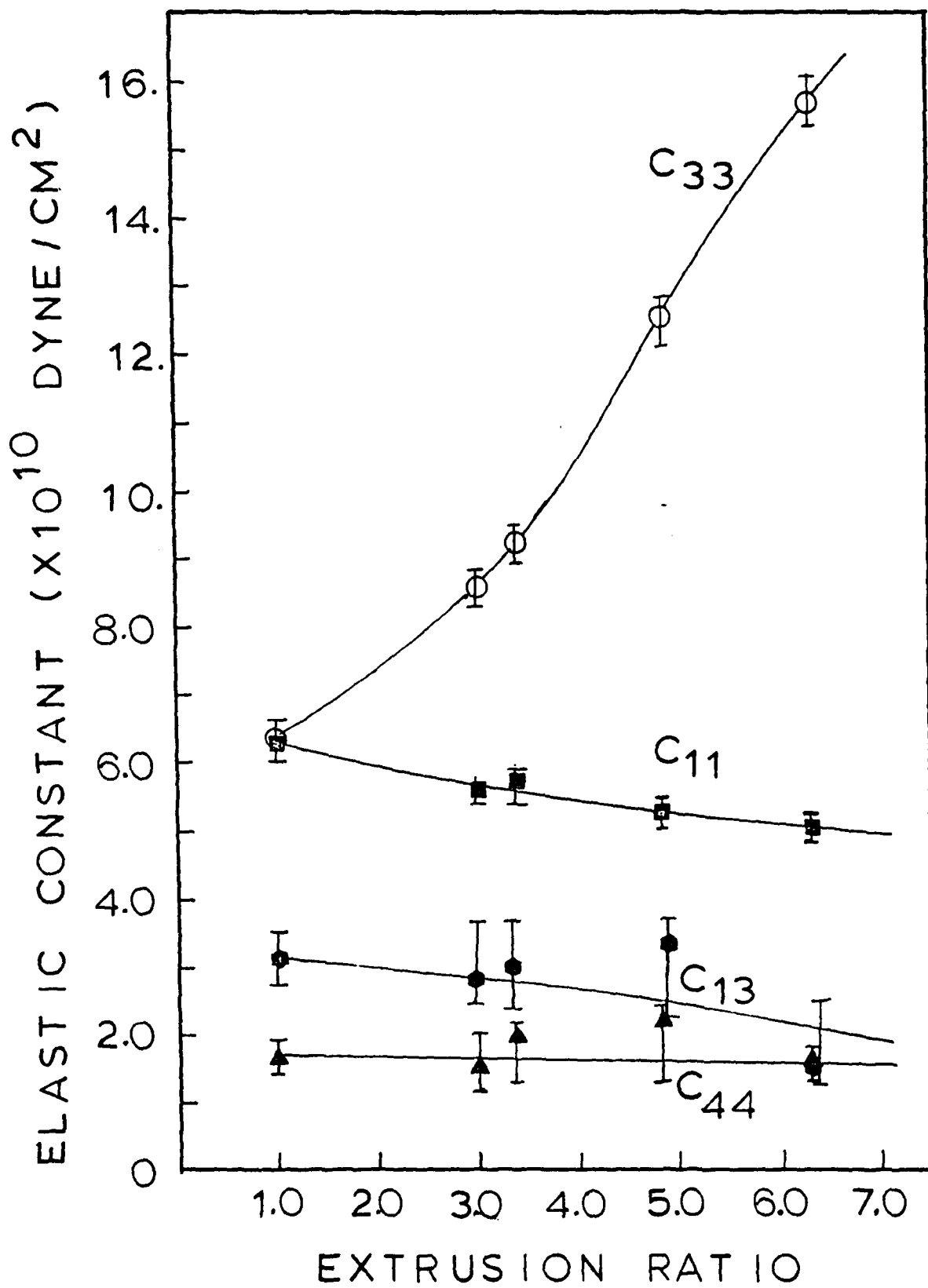
BRILLOUIN FREQUENCY (GHZ) Fig. 1

Fig. 2

x(zz)ỹ
Θ=120°

x(zz)y
Θ=90°

BRILLOUIN   FREQUENCY   (GHZ)

Fig. 11

Fig. 5
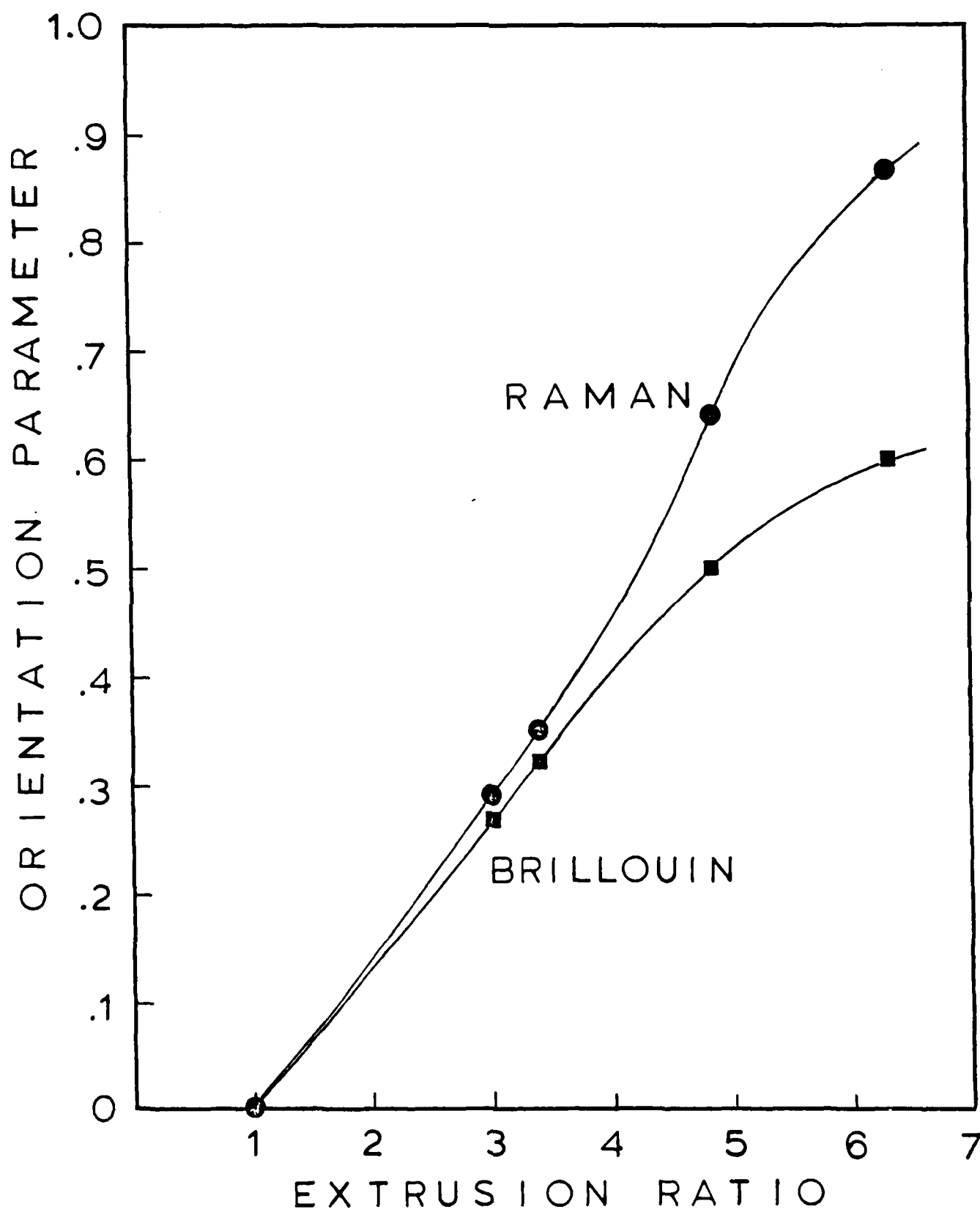
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